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Structure of medium-range order in molten Al-Fe alloy①

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[Abstract] The molecular-dynamics (MD) simulation was carried out to investigate the structure of medium-range order (MRO) of a liquid Al_5Fe_2 alloy. Prepeak is observed in the structure factor $S(Q)$, which is considered as the signature of MRO. Results from MD simulation and experiment agree well with each other, which proves reliability of the simulation. It is found from the calculated Ashcroft-Langreth structure factors that there exists strong interactional force between atom Al and Fe, which results in the great concentration fluctuation, i. e. the chemical order, in the liquid Al_5Fe_2. Both the chemical order parameter, α, and the Bhatia-Thornton(BT) structure factors indicate the preference for unlike-neighbor bonds. It is seen from the low-Q domain of $S(Q)$ and the concentration-concentration structure factor $S_{CC}(Q)$ that the prepeak mainly comes from the first peak of $S_{CC}(Q)$. The structural model, which reflects the characteristic of MRO, is also constructed .

[Key words] Al-Fe alloy; MD simulation; medium-range order; structure factor; prepeak
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1 INTRODUCTION

In recent years, medium-range order in liquids and amorphous solids is a subject of much interest[1~5]. Senda[6] investigated the ionic structure of liquid $Na_{0.8}Pb_{0.2}$ and $Na_{0.5}Pb_{0.5}$ alloys with *ab initio* molecular-dynamics simulations, and a medium-range order of Pb ions was seen in the liquid $Na_{0.8}Pb_{0.2}$ alloy. It is found from the calculated partial and total structure factors that the ordering of Pb ions leads to the first sharp diffraction peak (FSDP) of the total structure factors. In fact, it is difficult to get specific information on MRO in non-crystalline materials from the experimental structural measurements. However, a variety of techniques have allowed several types of characteristic structural order to be identified and their origin elucidated. The FSDP in the structure factor $S(Q)$ is often considered as the signature of MRO for some amorphous solids and liquids. It occurs in the low-Q domain (10~ 20 nm^{-1}) of $S(Q)$. Some Al-based alloy liquids, for example, the molten $Al_x[Mn_y(FeCr)_{1-y}]_{1-x}$[7] and $Al_{80}Ni_{20}$[8], exhibit a prepeak in both total and partial structure factors. For the FSDP, Cervinka[9] once put forward his doubt, he thought the name of FSDP was a misleading, because it is neither sharp, nor has it anything in common with diffraction, so he suggested that a first scattering peak (FSP) should be more appropriate in this case.

The structure origin of the FSDP is still a subject of considerable dispute. Sadigh[10] and Dzugutov[11] analyzed the origin of medium-range structure order in a simple monatomic liquid by MD simulation, they considered that a prepeak in the structure factor could be interpreted as chemical ordering in a mixture of atoms and atom-size vacancies. Elliott[12] also regarded the FSDP as a chemical-order prepeak due to interstitial volume around cation-centered structural units. The models for the MRO[13] have been proposed in Ag and Li borate glasses, and a conclusion was drawn that the MRO structure consists of a continuous network of BO_4 and BO_3 units.

Some papers[14, 15] on the structural features of liquid Al-Fe alloy were reported based on the experimental researches and the prepeak was found in its structural factor. However, few of them profoundly traced its origin. In this work, we give a thorough study on the MRO of liquid Al-Fe alloy and the theoretical explanation of the prepeak.

2 SIMULATION PROCESS ON LIQUID Al_5Fe_2 ALLOY

The MD simulation method was adopted under constant pressure and constant temperature, using the second-moment approximation of the tight-bonding (TB-A) potential scheme[16]. The total cohesive energy of the system, E_c, consists of two parts, band energy and repulsive energy, as following:

$$E^i_B = -\left\{ \sum_j \xi^2_{\alpha\beta} \exp\left[-2q_{\alpha\beta}\left(r_{ij}/r_0^{\alpha\beta} - 1\right)\right]\right\}^{1/2} \tag{1}$$

and

$$E^i_R = \sum_j A_{\alpha\beta} \exp\left[-p_{\alpha\beta}\left(r_{ij}/r_0^{\alpha\beta} - 1\right)\right] \tag{2}$$

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so $E_c = \sum_i (E_R^i + E_B^i)$. Where r_{ij} represents the distance between atoms i and j; and $r_0^{\alpha\beta}$ is the first-neighbors distance in the lattice; ξ, q, A, p are the model parameters, respectively.

The simulation was performed in a cubic cell of 490 atoms at zero external pressure. The internal pressure can be obtained from the Virial theorem[17]. Periodic boundary conditions were assumed to simulate the bulk geometry. The equations of motion were solved by the Verlet algorithm[18] with a time interval of 5 fs. Here the damped-force method was used to decrease temperature by forcing bath temperature to change linearly at every time interval.

3 RESULTS AND DISCUSSION

The results of X-ray diffraction on the sample of Al_5Fe_2 are shown in the Fig. 1. It can be seen that the position of the main peak (28.75 nm^{-1}) for Al_5Fe_2 at 1 545 K agrees well with that (28.61 nm^{-1}) at 300 K, and also agrees with those of two strongest peaks (29.78 nm^{-1}, 30.65 nm^{-1}) given by international standard spectrum[19], which suggests that the structure of liquid Al_5Fe_2 be similar with that of solid, to a certain extent. In general, the liquid alloy presents the characteristic of short-range order (SRO), and the solid alloy presents not only short-range order but also long-range order. For the diffraction curve the SRO is represented by the fact that there is a sharp main peak on the low-Q domain (25~ 35 nm^{-1}) of $S(Q)$ in the reciprocal space, and in real space SRO structure is reflected by the fact that there is an obvious first peak in pair correlation function $g(r)$. The comparability of the main peak between liquid and solid in the diffraction curve generally means that there exists the comparability in the topology structure between them, but it doesn't reflect the comparability of the chemical order. It is worth noticing from Fig. 1 that there exists a prepeak in the small-Q region (14.9 nm^{-1}) for liquid Al_5Fe_2. There is a sharp peak at 16nm^{-1} when temperature is 300 K, and there also exist three stronger diffraction peaks at Q = 12.82, 16.49, 19.6 nm^{-1}, respectively, according to the international standard spectrum. So it is obvious that there must be the definite atom arrangement in the liquid Al_5Fe_2. When solid changes into liquid, the peak before the main peak broadens and gradually evolves into the prepeak.

The partial PCF $g_{ij}(r)$[20] calculated by our MD simulation, the probability of finding an atom in the range from r to $r+\Delta r$, is conventionally defined by

$$g_{ij}(r) = \frac{l^3}{N_i N_j} \frac{\sum_{\alpha=1}^{N_1} N_{\alpha j}(r)}{4\pi r^2 \Delta r} \tag{3}$$

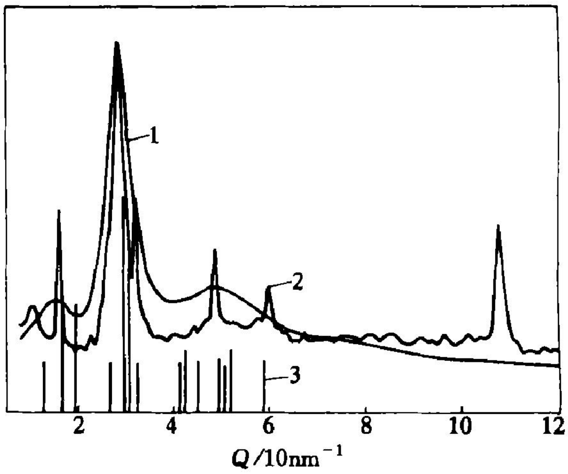

Fig. 1 X-ray diffraction patterns of Al_5Fe_2 alloy
1 —Liquid (1 545 K); 2 —Solid (300 K);
3 —Standard

where l is the cell length of the box in the simulation, N_i and N_j are the respective numbers of atoms i and j in the system and $N_{\alpha j}$ is an averaged number of j-type atoms around i-type atoms in the sphere shell ranging from r to $r+\Delta r$, Δr is the step of the computation. So the total PCF is obtained by

$$g(r) = \sum_i \sum_j W_{ij} g_{ij}(r) \tag{4}$$

$$W_{ij}(s) = c_i c_j \frac{f_i(s) f_j(s)}{[f(s)]^2} \tag{5}$$

and

$$[f(s)]^2 = \left[\sum_i^N c_i f_i(s) \right]^2 \quad i = 1, 2, 3, \cdots N \tag{6}$$

where c_i, c_j are the concentrations of i-type atoms and j-type atoms, respectively; $f_i(s)$, $f_j(s)$ are the respective scattering factors of i-type atoms and j-type atoms. According to Fourier transformation of PCF, we can get the structure factor $S(Q)$ in reciprocal space as following:

$$S(Q) = 1 + \rho \int_0^\infty 4\pi r^2 [g(r) - 1] \frac{\sin Qr}{Qr} dr \tag{7}$$

Here ρ is the number density.

The structure factors both calculated by MD simulation and determined from X-ray diffraction experiment are shown in Fig. 2. It shows that both of them agree well with each other except that the main peak of experiment is a bit higher than that of MD simulation. There are obvious prepeaks in the low-Q domain for both of $S(Q)$. The careful measurements of the prepeak in Al_5Fe_2 have shown that it can be approximated well by a Lorentzian curve. To evaluate the half-width ΔQ of the prepeak, we apply a Lorentzian approximation fitted to the small-Q domain of $S(Q)$[21]:

$$S(Q) \cong \Delta Q / \left[(Q - Q_{PP})^2 + \Delta Q^2 \right] \tag{8}$$

where Q_{PP} is the position of the prepeak. Then the size of atom clusters, D, reflected by the prepeak is gained by Scherrer formula

$$D \approx 2\pi / \Delta Q \tag{9}$$

The results are shown in Table 1. According to the viewpoint of Elliott[22], the size range of MRO is between 0.5 nm and 2.0 nm. Based on this, we can draw a conclusion that there exists the structure of MRO in the liquid Al_5Fe_2 alloy.

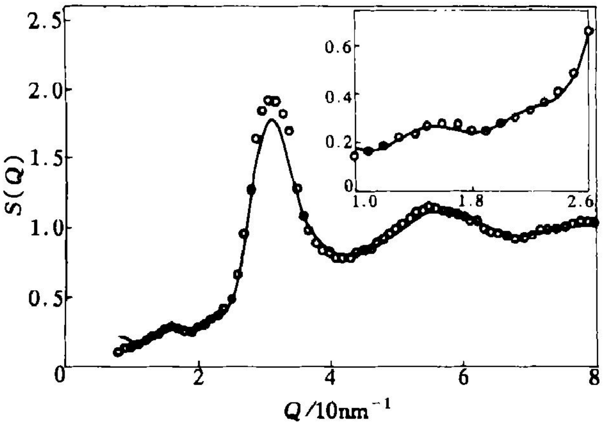

Fig. 2 Total structure factor of liquid Al_5Fe_2 at 1 545 K

Solid line—MD simulation; ○—Experiment

Table 1 Position (Q_{pp}), half-width (ΔQ) of prepeak and size (D) of clusters for liquid Al_5Fe_2

T/K	Q_{pp}/nm^{-1}	ΔQ/nm^{-1}	D/nm
1 545	~ 14.9	~ 4.64	~ 1.384

In order to discuss the MRO of Al-Fe alloy, it is significative to investigate the number-number structure factor $S_{NN}(Q)$ and the concentration-concentration structure factor $S_{CC}(Q)$ from the Bhatis-Thornton(BT) formalism[23], which are defined as a function of wave vector Q by

$$S_{NN}(Q) = c_i S_{ii}(Q) + 2(c_i c_j)^{1/2} S_{ij}(Q) + c_j S_{jj}(Q) \tag{10}$$

$$S_{CC}(Q) = c_i c_j [c_j S_{ii}(Q) - 2(c_i c_j)^{1/2} S_{ij}(Q) + c_i S_{jj}(Q)] \tag{11}$$

where c_i, c_j, are the concentration of the i-type species and j-type species, respectively; $S_{ii}(Q)$, $S_{ij}(Q)$ and $S_{jj}(Q)$ are the partial structure factors in the Ashcroft-Langreth(AL) form, respectively. We have calculated the AL partial structure factors as following

$$S_{ij}(Q) = \frac{1}{(N_i N_j)^{1/2}} \langle \sum_{m=1}^{N_i} \sum_{n=1}^{N_j} \exp[iQ(r_m - r_n)] \rangle \tag{12}$$

where r_m, r_n are the positions of Al and Fe obtained by our MD simulation, respectively. The bracket $\langle \cdots \rangle$ means the time average.

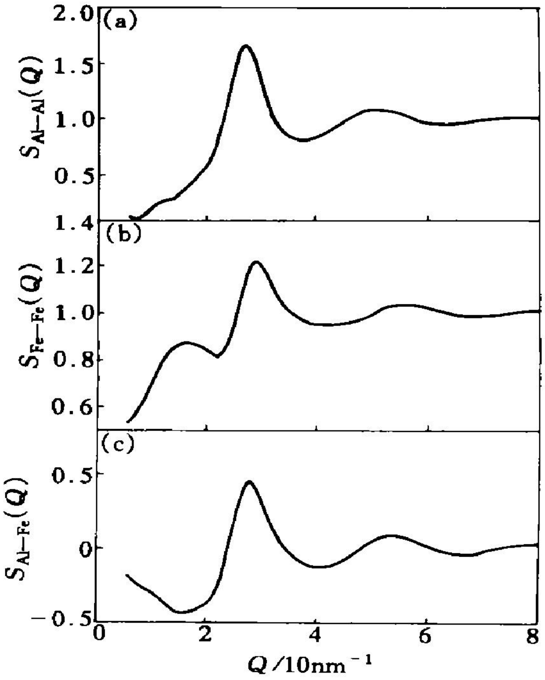

Fig. 3 Ashcroft-Langreth partial structure factors at 1 545 K

The calculated AL structure factors represented in Fig. 3 display a significant prepeak and preminimum in the minority-minority (Fe—Fe) and heteroatomic (Al—Fe) partial structure factors, respectively, indicating superstructure effects resulting from the preference of heteroatomic interaction in the liquid. As for $S_{Al-Al}(Q)$, there don't exist the prepeak and preminimum, which implies that the superstructure in the liquid is mainly contributed to $S_{Fe-Fe}(Q)$ and $S_{Al-Fe}(Q)$. And this is mainly related to the electronic structure and orbital hybridization of the system.

In Fig. 4, we show the total structure $S(Q)$, the BT structure factors $S_{NN}(Q)$ and $S_{CC}(Q)$ for the liquid Al_5Fe_2 at 1 545 K. In the prepeak region the concentration (C) and number(N) fluctuations clearly correlate. It is seen that the prepeak($Q = 14.9$ nm^{-1}) in the low-Q region and the first peak($Q = 28.5$ nm^{-1}) of the $S(Q)$ come from the first peak ($Q = 14.5$ nm^{-1}) of $S_{CC}(Q)$ and the first main peak ($Q = 28.5$ nm^{-1}) of $S_{NN}(Q)$, respectively, which suggests the prepeak originate much possibly from the concentration fluctuation. There also exists a prepeak in the low-Q domain of $S_{NN}(Q)$, whose position is very close to that of the first peak of $S_{CC}(Q)$, which once again indicates that the chemical ordering of Al-Fe should be responsible for the MRO structure in the liquid Al_5Fe_2 alloy.

The partial pair correlation functions $g_{ij}(r)$ are displayed in Fig. 5. The value of $g_{Al-Fe}(r)$ is the highest among the three partial PCFs, which indicates that there exists the stronger interactional force for atoms Al and Fe as described previously, and that most of Fe atoms are combined with Al atoms in the liquid Al_5Fe_2. Table 2 lists the calculated values of r_{ij} for each of the first peaks in g_{Al-Al}, g_{Al-Fe} and g_{Fe-Fe}. This gives an indication of the average first-neighbor i—j bond lengths in the liquid alloy. From Table 2, it can be seen that Al — Fe bonds are significantly shorter than

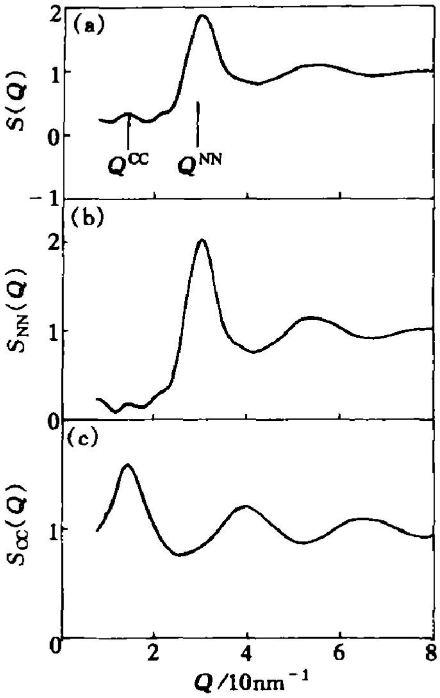

Fig. 4 Bhatia-Thornton partial structure factors at 1 545 K

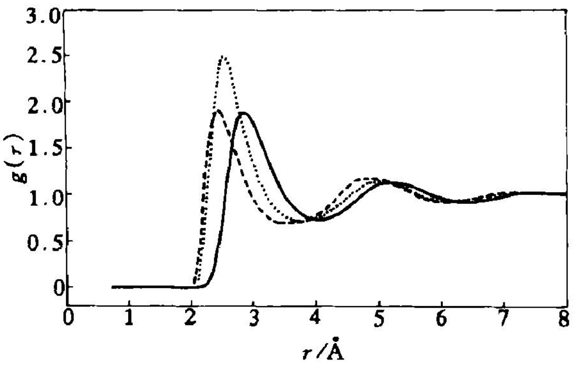

Fig. 5 Partial pair correlation functions of liquid Al_5Fe_2

Solid line—$g_{Al-Al}(r)$; Dotted line—$g_{Al-Fe}(r)$; Dashed line—$g_{Fe-Fe}(r)$

Table 2 Calculated first peak of $g_{ij}(r)$, nearest-neighbor distances (r), coordination numbers (N), and chemical order parameters (α) for liquid Al_5Fe_2 at 1 545 K

Bond	$g_{ij}(r)$	r/nm	N	α
Al—Al	1.95	0.283	8.46	—
Al—Fe	2.51	0.251	3.95	-0.114
Fe—Al	2.51	0.251	9.89	-0.163
Fe—Fe	1.88	0.244	2.01	—

both Al—Al and Fe—Fe bond lengths, and this means there is a further indication of the strong preference for heteroatomic nearest-neighbor bonds in Al-Fe alloys, which is determined by quantum mechanics calculation. As discussed by Maret[8], we can compute values for the partial coordination numbers in the different coordination shells around Al and Fe atoms, which are obtained by integrating the partial pair correlation functions out to the distance corresponding to the first maximum and then by doubling it as in the following equation

$$N_{ij} = 2\rho_j \int_0^{r_{ij}} 4\pi r^2 g_{ij}(r)\,dr \tag{13}$$

where ρ_j is the number density of j-type atoms and r_{ij} is the first peak position of the $g_{ij}(r)$, N_{ij} is the average number of j-type species surrounding i-type species within the first coordination shell of the liquid. The results calculated are also shown in Table 2. As described previously, the partial coordination number of Fe—Al is the biggest among them, which indicates there exists the strong chemical order in the liquid.

In terms of N_{ij}, it is possible to define CSRO parameters[24] which is defined by

$$\alpha_{ij} = 1 - \frac{N_{ij}}{c_j N_i} \tag{14}$$

where c_j is the concentration of the j-type species and N_i ($N_i = N_{ii} + N_{ij}$) is the total coordination number around the i-type species. The values of α_{ij} indicate the different preference for the neighbor bonds. $\alpha_{ij} = 0$ indicates that there is no chemical order in the liquid; $\alpha_{ij} > 0$ indicates a preference for like-neighbor bonds and $\alpha_{ij} < 0$ means a tendency for the unlike-neighbor bonds. In our simulation $\alpha_{Al-Fe} = -0.114$ and $\alpha_{Fe-Al} = -0.163$, which once again indicates the preference for unlike-neighbor bonds. In other words, there exists the stronger chemical order in the liquid as discussed previously. It is the chemical order between atoms Al and Fe that plays an important role in the origin of prepeak of $S(Q)$ in liquid Al_5Fe_2 alloy.

According to the prepeak origin and the calculated cooperation number between Al and Fe atoms, the model structure of the clusters in the liquid was constructed (shown in Fig. 6). For liquid Al_5Fe_2, Fe is the minority and there exists the preference for unlike-neighbor bonds , so its nearest neighbors are mostly occupied

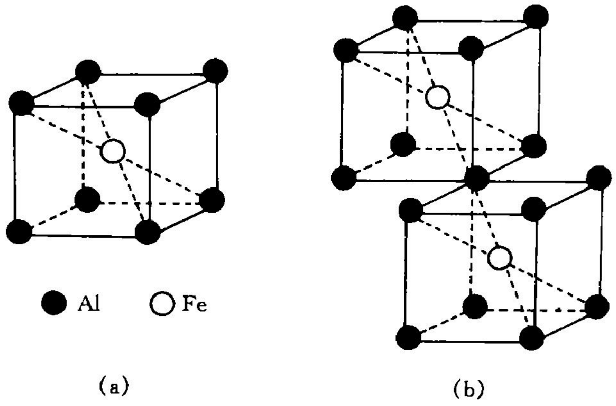

Fig. 6 Unit of structure model for liquid Al_5Fe_2

by Al atoms, which can be confirmed from the cooperation number of Al—Fe listed in Table 2. As also can be seen from Table 2, $d_{\mathrm{Al-Fe}}$ is almost $\sqrt{3}/2$ times as much as that of $d_{\mathrm{Al-Al}}$. Therefore, it is assumed that, in this model (Fig. 6(a)), eight Al atoms form a cube with an edge of 0.283 nm, whose center is occupied by a Fe atom. Then the $d_{\mathrm{Al-Fe}}$ is 0.251 nm, very close to the value of 0.248 nm[14]. If another unit with the same structure is connected with this one and shares one Al atom along a body diagonal (Fig. 6(b)), the distance $d_{\mathrm{Fe-Fe}}$ between these two units is 0.502 nm. Moreover, it can be seen from the size of the cluster that a cluster contains about 4~ 8 cubic structure units.

4 CONCLUSIONS

The molecular dynamics simulation was carried out for liquid $\mathrm{Al_5Fe_2}$ at 1 545 K (above the liquidus) and the structure of the medium-range order in the liquid was studied. The prepeak, the signature of the MRO, observed in the MD simulation is in good agreement with that from experiment. It is found from the detailed analysis of partial structure factors and partial correlation functions that there exists the stronger interactional force between atoms Al and Fe, which is approved by the calculation of quantum mechanics. The concentration-concentration structure factor $S_{\mathrm{CC}}(Q)$ shows that there is the great concentration fluctuation in the liquid, and it is considered that there is the stronger chemical order in it. The chemical order parameter, α, also indicates the preference for unlike-neighbor bonds in the liquid. It is seen from $S(Q)$ and $S_{\mathrm{CC}}(Q)$ that the prepeak of $S(Q)$ comes from the first peak of $S_{\mathrm{CC}}(Q)$, so it is inferred that the chemical order leads to the prepeak of the total structure factor. Based on above discussion, the structure model for MRO was constructed.

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